

I. The Polymerization of Asymmetrical
Diaryl and Arylalkylethylenes.

II. Studies in the Quinoidation of
Arylalkylchloromethanes.

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
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Joseph Dennis Ryan
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To doctor L. C. Anderson who so kindly assisted with the spectrographic work, the author expresses his appreciation.



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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE POLYMERIZATION OF ASYMMETRICAL
DIPHENYLETHYLENE. THE PREPARATION OF
1,1,3-TRIPHENYL-3-METHYLHYDRINDENE

By C. S. SCHOEPFLE AND J. D. RYAN¹

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Bergmann and Weiss, in a paper recently published,² have shown that the saturated dimer of asymmetrical diphenylethylene is 1,1,3-triphenyl-3-methylhydrindene and not tetraphenylcyclobutane, as previously supposed, and have stressed the importance of this fact in connection with the views of Staudinger and others on the mechanism of polymerization and the structure of high molecular weight compounds. In a study of the properties of this saturated dimer in this Laboratory, its identity has been established, independently, from its oxidation products. Our investigation, which is still in progress, is concerned chiefly with the mechanism of the reaction by which triphenylmethylhydrindene and other indenenes are formed, but the work has paralleled that of Bergmann and Weiss in many respects and therefore it is considered advisable to publish the results which have been obtained at this time.

Polymerization of asymmetrical diphenylethylene (I) by the use of catalysts yields two dimeric compounds, one unsaturated (III) and the other saturated (XII). The unsaturated dimer, m. p. 113°, was prepared first by Hildebrand³ and shown by Lebedev⁴ to be 1,1,3,3-tetraphenyl-1-butene,

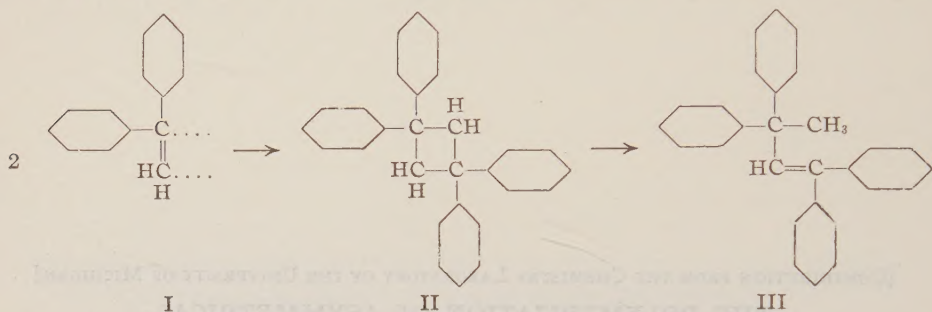
¹ This paper represents part of a dissertation to be submitted to the Graduate School by Mr. Ryan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

² Bergmann and Weiss, *Ann.*, 480, 49 (1930).

³ Dissertation by Hildebrand, Strassburg, 1909.

⁴ Lebedev, Andreevskii and Matiushkina, *Ber.*, 56, 2349 (1923).

which structure was confirmed by Schlenk and Bergmann.⁵ The formation of this compound may be explained by assuming that two molecules of asymmetrical diphenylethylene combine under the influence of catalysts such as sulfuric acid, iodine, stannic chloride, etc., to give 1,1,3,3-tetraphenylcyclobutane (II), which being unstable rearranges to 1,1,3,3-tetraphenyl-1-butene (III). The intermediate product cannot be 1,1,4,4-



tetraphenylcyclobutane, since it appears from the work of Schlenk and Bergmann⁶ that this compound, prepared by the action of mercury on 1,4-disodium-1,1,4,4-tetraphenylbutane, reverts to diphenylethylene.

The saturated dimer, m. p. 143°, was prepared first by Lebedev,⁴ who obtained a mixture of the two isomers by treating diphenylethylene with concentrated sulfuric acid or with fuller's earth. He concluded that this compound was tetraphenylcyclobutane, since it did not add bromine nor react with ozone, and gave only benzophenone on oxidation. The compound is very stable toward oxidation and Bergmann and Weiss state that long treatment with a considerable excess of chromic acid in acetic acid oxidized only a part of the material and that this part was completely destroyed. By regulating the conditions of the oxidation, however, it is possible to control the reaction so that over a 40% yield of the crude oxidation product is obtained. This product contains a large number of acids and ketones of which about ten have been isolated in pure form. Only two of these were readily identified, namely, benzoic acid and *o*-dibenzoylbenzene. In addition, benzophenone was isolated as the oxime in small amounts, substantiating the observation of Lebedev. The two latter oxidation products were sufficient to establish the identity of the hydrocarbon, since of the various structures which might be assigned to a dimer of diphenylethylene, only one, namely, 1,1,3-triphenyl-3-methylhydrindene could give both *o*-dibenzoylbenzene and benzophenone on oxidation and could readily be formed by the rearrangement of 1,1,3,3-tetraphenyl-1-butene, which rearrangement had been effected by Lebedev⁴

⁵ Schlenk and Bergmann, *Ann.*, **463**, 239 (1928).

⁶ Ref. 5, p. 7.

with fuller's earth at high temperature and with stannic chloride plus hydrochloric acid at room temperature in our work. A synthesis of this hydrindene was in progress at the time when Bergmann and Weiss² reported their excellent synthesis, which removed any possible doubt concerning its structure.

1,1,3-Triphenyl-3-methylhydrindene can be readily prepared in practically quantitative yield by adding anhydrous stannic chloride to a benzene solution of methyldiphenylchloromethane, obtained by the action of dry hydrogen chloride on the corresponding carbinol, and allowing the mixture to stand at room temperature for one week. The reaction is apparently a general one and has been extended to several other carbinol chlorides. For example, dimethylphenylchloromethane gave the dimer, m. p. 52.5°, first described by Grignard,⁷ and dimethyl-*p*-tolylchloromethane and dimethyl- α -naphthylchloromethane gave compounds melting at 122 and 199°, respectively.⁸ The structures of these compounds remain to be proved. Zinc chloride, ferric chloride, antimony pentachloride and aluminum chloride have been used in the reaction in place of stannic chloride, and it is probable that other agents such as boron trichloride and titanium tetrachloride will also be effective.

Inasmuch as tetraphenylbutene can be rearranged to the hydrindene by concentrated sulfuric acid at room temperature, it seems probable that the former is an intermediate step in the preparation of the latter compound from diphenylethylene. As suggested by Bergmann and Weiss, the rearrangement of the unsaturated dimer would consist in the addition of the sulfuric acid to the double bond and the subsequent removal of the acid to form the stable five-membered ring. The unsaturated dimer may also be rearranged by means of stannic chloride, provided hydrogen chloride is present. A benzene solution of this compound in the presence of stannic chloride showed no appreciable rearrangement after one week at room temperature, but when the solution was partially saturated with hydrogen chloride, the rearrangement to the saturated dimer was practically complete in the same period of time. Again, diphenylethylene in benzene solution under the influence of stannic chloride polymerized almost exclusively to the unsaturated dimer, while in the presence of hydrogen chloride the saturated isomer was formed. These results apparently favor the theory that an intermediate compound is formed by the addition of hydrogen chloride to the unsaturated dimer, which compound then reacts to give the hydrindene, but there is some evidence which points to a different mechanism of reaction when stannic chloride is used.

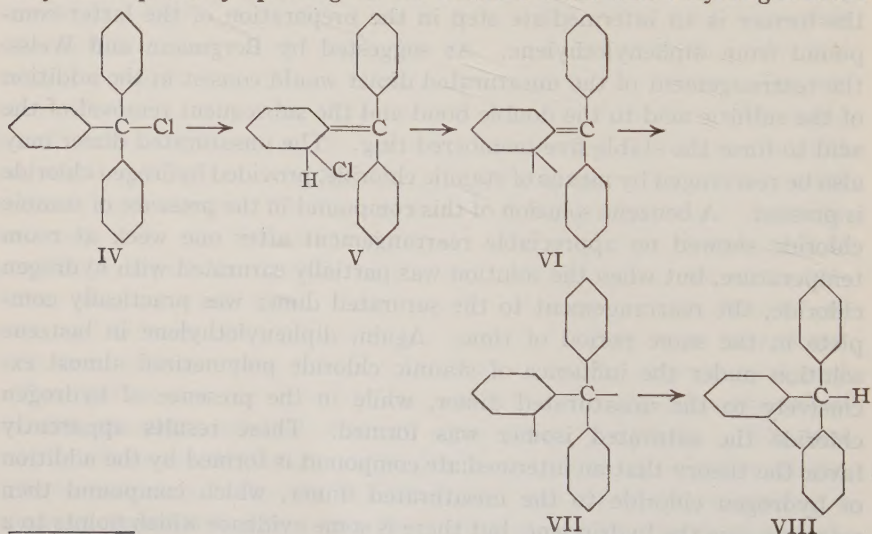
If the preparation of 1,1,3-triphenyl-3-methylhydrindene from methyl-

⁷ Grignard, "Ann. de l'Univ. of Lyon," 1901, p. 57; *Ann. chim. phys.*, [7] 24, 485 (1901).

⁸ These compounds were prepared by R. F. Ruthruff.

diphenylchloromethane is compared with the preparation of fluorenes from triarylmethyl halides, it is found that the two reactions have much in common. In each case the product is an indene derivative, and in each case the same reagents may be used to bring about the reaction, namely, stannic chloride, aluminum chloride, zinc chloride, etc. These reagents incidentally give definite colored addition products with the triarylmethyl halides which have been shown to be quinonoid in character.⁹ The ease with which fluorenes are formed from triarylmethyl halides varies greatly with different individuals. Triphenylmethyl chloride and bromide give phenylfluorene (VIII) only upon heating above 200°. ¹⁰ Phenyl- α -naphthofluorene, however, may be prepared by refluxing an acetic acid solution of α -naphthylidiphenylcarbinol in the presence of a small amount of hydrochloric acid, sulfuric acid, zinc chloride, etc.;¹¹ the solution first acquires a dark green color which rapidly disappears, indicating that the intermediate product is a quinonoid chloride, sulfate, etc. Di- α -naphthylphenylmethyl chloride or bromide is still more reactive. These halides give addition products of a deep purple color with stannic, aluminum, ferric, zinc and mercuric chlorides, which are unstable and decompose within a short time at room temperature with the formation of di- α -naphthofluorene.¹²

The reaction, for example, in the case of triphenylchloromethane, probably takes place by splitting off the chlorine atom and a hydrogen atom



⁹ Gomberg, *Ber.*, 40, 1847 (1907); 42, 406 (1909); Anderson, *THIS JOURNAL*, 52, November, 1930.

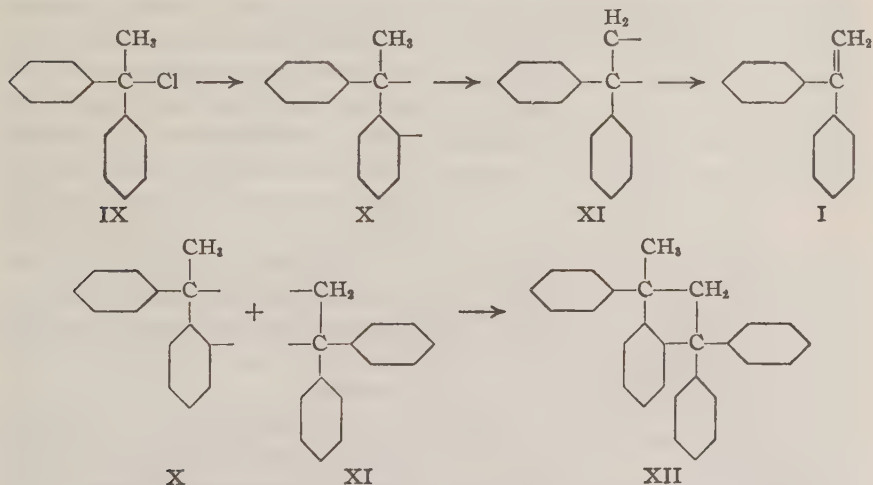
¹⁰ Hemilian, *Ber.*, 7, 1208 (1874); 11, 837 (1878); E. and O. Fischer, *Ann.*, 194, 257 (1878); Schwarz, *Ber.*, 14, 1522 (1878).

¹¹ Ullmann and Mourawiew-Winogradoff, *ibid.*, 38, 2213 (1905).

¹² Schoepfle, *THIS JOURNAL*, 44, 188 (1922).

from an ortho position in the ring to give an unstable intermediate product (VII) which rearranges to the stable fluorene (VIII). Since the reagents or the conditions used in the reaction result in quinoidation of the triarylmethyl halide, the formation of the intermediate compound (VII) may be postulated as being due to splitting off hydrogen chloride from the ortho quinonoid compound, (V), to give the quinonoid residue (VI), which would, of course, rearrange to the benzenoid configuration (VII). In general, the triarylmethyl halides assume the para-quinonoid form but some of the ortho-quinonoid form may also be present, and, indeed, certain compounds would be expected to assume the ortho-quinonoid form more readily than others, which might account for the greater ease with which naphthyl derivatives react in comparison with phenyl derivatives.

In the case of methyldiphenylchloromethane (IX), hydrogen chloride may be split off in accordance with the mechanism proposed above to give



the intermediate product (X), which then tends to rearrange not to methylfluorene but to asymmetrical diphenylethylene, a rearrangement which is not possible in the case of the triarylmethyl derivatives. Actually, however, the rearrangement does not proceed thus far, due to the coupling of the two intermediate products (X) and (XI) to give the stable triphenylmethylhydrindene.

Methyldiphenylcarbinol and concentrated sulfuric acid give a red color which is also characteristic of the addition compounds of methyldiphenylchloromethane with stannic chloride, aluminum chloride, ferric chloride, etc. In the polymerization of diphenylethylene to the hydrindene in the presence of stannic chloride and hydrochloric acid, and in the rearrangement of the unsaturated dimer under these conditions, the same red color always appears. In the absence of hydrochloric acid, the ethylene and the

unsaturated dimer give a light green color instead of the red color and in each case practically no hydrindene is obtained. In other words, it seems that the preparation of the hydrindene may be dependent on the formation

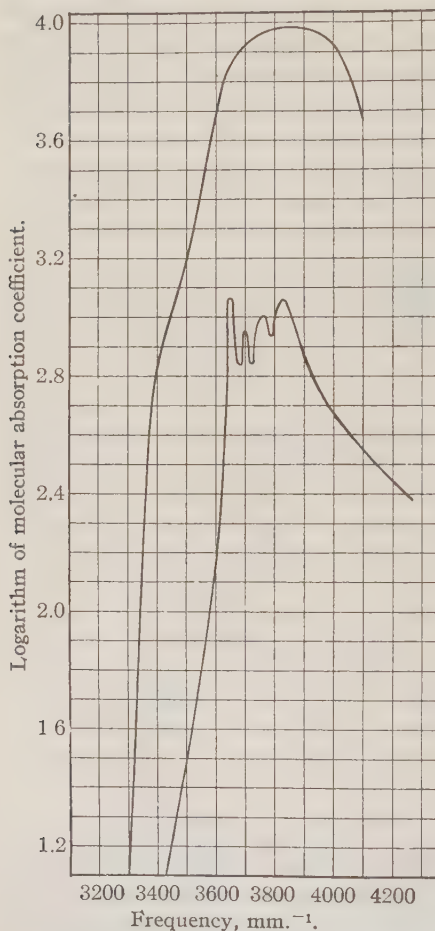


Fig. 1.—Upper curve, 1,1,3,3-tetraphenyl-1-butene; lower curve, 1,1,3-triphenyl-3-methylhydrindene.

of methyldiphenylchloromethane as the intermediate product. The formation of this compound is readily explainable with the ethylene which may add hydrochloric acid under the influence of the stannic chloride, and is also plausible in the case of the unsaturated dimer, which evidently dissociates readily to the ethylene, since Hildebrand³ found that bromine and nitric acid in boiling acetic acid react with the unsaturated dimer to give dibromodiphenylethylene and diphenylvinyl nitrite, respectively, while Lebedev⁴ found that with excess of ozone at 0°, diphenylethylene ozonide was obtained from the dimer. Moreover, it was observed that the unsaturated dimer in benzene solution and in the presence of stannic chloride depolymerized to an appreciable extent at room temperature.

An attempt was made to establish the identity of the red intermediate compound formed in the various reactions by means of absorption spectra in the visible region, using a Nutting photometer and a Hilger wave length spectrometer. The following solutions were investigated: (1) methyldiphenylcarbinol in concentrated sulfuric acid, (2) methyldiphenylchloromethane and stannic chloride in benzene, (3) diphenylethylene, stannic chloride and hydrochloric acid in benzene, and (4) tetraphenylbutene, stannic chloride and hydrochloric acid in benzene. All showed a rapid increase in absorption in the violet region and gave an indication of a band with its peak near the edge of the visible part of the spectrum. The location of this peak could not be definitely determined, due to the limitations

of the apparatus at wave lengths below 4500 Å. Spectrographic measurements of the absorption spectra of these solutions are to be undertaken in order to obtain this information.

In many of our preliminary experiments mixtures of the unsaturated and saturated dimers of diphenylethylene were obtained and it was desirable to determine the amount of each isomer present, but the separation by means of fractional crystallization was tedious and unsatisfactory. The mixtures did not melt sharply and did not crystallize readily on cooling, so that the melting point and solidification point were of no value for this purpose. The index of refraction of a concentrated solution of the material could not be used, due to the fact that the indices of refraction of the pure isomers were too nearly alike. The absorption curves of the two dimers are quite different though, as will be seen from Fig. 1, and therefore the composition of a mixture could be quite accurately determined from the molecular absorption coefficient at frequencies between 3425 and 3600. The absorption curves should also prove of value in establishing the structure of other indene derivatives which are not readily synthesized.

The measurements of the absorption spectra were made with a Judd-Lewis sector photometer and a Hilger quartz spectrograph, size C, by Dr. L. C. Anderson of this Laboratory, for whose assistance we wish to express our appreciation.

Experimental

Methyldiphenylchloromethane.—This compound was prepared by treating a benzene solution of the carbinol with dry hydrochloric acid gas at a temperature below 10° in the presence of anhydrous calcium chloride to remove the water formed in the reaction. Attempts to isolate the chloride by concentrating the solution gave a colorless oil which could not be crystallized, although an analysis for chlorine showed that no appreciable decomposition had taken place. A sample of the chloride was prepared in low-boiling petroleum ether, the solvent removed under reduced pressure at 0° and a stream of dry air passed through the residual oil to remove traces of hydrochloric acid. On analysis, 16.0% of chlorine was obtained, the calculated value being 16.4%. At room temperature the chloride decomposes slowly to give the ethylene and hydrochloric acid, a small amount of the unsaturated dimer of diphenylethylene being formed.¹³

1,1,3-Triphenyl-3-methylhydrindene.—Twenty-five grams of methyldiphenylcarbinol was dissolved in 250 cc. of benzene and converted into the chloride as described above. Ten grams of anhydrous stannic chloride was then added and the solution maintained below 10° for several hours, after which it was allowed to stand at room temperature. Upon the addition of the stannic chloride, the solution acquired a deep red color which gradually faded to a light brown. After one week it was washed thoroughly with water, dried and concentrated, and the residue dissolved in absolute alcohol, from which the triphenylmethylhydrindene was obtained in colorless crystals melting at 143°; yield, 95–97%. If the reaction is stopped after one day at room temperature, the yield is about 80%. An attempt to accelerate the reaction by heating on the steam-bath gave a decreased yield due to the formation of diphenylethylene and the unsaturated dimer.

¹³ Blicke and Powers, *THIS JOURNAL*, **51**, 3383 (1929).

Saturated Dimer of α -Methylstyrene.—This compound was prepared from dimethylphenylcarbinol by the method described above. The oily product from the concentration of the solution was rubbed with a small amount of alcohol, whereby a solid separated which was filtered and recrystallized. An additional amount of the product was obtained by distilling the oily residue and crystallizing the fraction which boiled at 128–135° at 3 mm. from alcohol. The combined yield of the dimer was 88% and the melting point 52°. The same compound is obtained if the stannic chloride used in the reaction is replaced by ferric chloride, aluminum chloride, antimony pentachloride or zinc chloride; stannic chloride and antimonious chloride have the advantage over the other reagents in that they are soluble in benzene. Staudinger and Breusch¹⁴ have previously prepared this compound in 72% yield by the action of stannic chloride on α -methylstyrene.

Oxidation of 1,1,3-Triphenyl-3-methylhydrindene.—Five grams of the hydrocarbon was dissolved in 100 cc. of glacial acetic acid and 25 g. of chromic acid was cautiously added. The reaction was allowed to proceed rapidly with just enough cooling to prevent it from becoming violent, and was usually complete in about half an hour. After one hour the solution was poured into water, cooled to 0° with ice and partially neutralized by adding a solution of 50 g. of sodium hydroxide, which seemed to change the character of the precipitate so that it was easier to filter. The product was washed with water on the filter and air dried. No further material could be recovered from the filtrate by extraction with ether.

The crude oxidation products obtained from a number of runs were combined and extracted with hot water. From the water solution a small amount of oil was obtained by extraction with ether and evaporation of the solvent. Crystallization of the oil from alcohol gave a mixture of colorless, thin plates which after recrystallization melted at 95°, and colorless serrated tables which melted at 146°. A small amount of benzoic acid was obtained by sublimation of that portion of oil which failed to crystallize.

The residual oxidation product was then treated under rapid stirring with warm 25% sodium hydroxide solution and the mixture allowed to settle. The supernatant liquid was decanted or siphoned off and the operation repeated twice to insure removal of all of the alkali-soluble material. The product which was insoluble in alkali was steam distilled and the distillate extracted with ether. A small amount of oil was obtained from the ether solution which upon crystallization from alcohol gave the 146° compound along with long thin colorless needles which melted after recrystallization at 279°. The portion of oil which did not crystallize was treated with hydroxylamine hydrochloride and deposited benzophenone-oxime, which was identified by a mixed melting point. Extraction with ether of the non-volatile residue from the steam distillation, evaporation of the solvent and crystallization of the product from alcohol gave an additional quantity of the 146° compound.

The material soluble in 25% sodium hydroxide solution was precipitated with dilute hydrochloric acid, and the precipitate washed with water and air dried. The yield of this product was 40% of the weight of hydrocarbon oxidized. The material was stirred with a slight excess of dilute sodium hydroxide solution in which about 20% remained insoluble. This was filtered, washed with water, air dried and dissolved in alcohol. Two compounds were recovered from the solution, the 146° compound and large colorless needles which after recrystallization melted at 120°. The solution obtained by redissolving the oxidation product in dilute sodium hydroxide solution was treated with ether and the extracted material crystallized from alcohol. More of the 120° compound was obtained and also a small amount of small colorless needles which melted at 295° after recrystallization. The alkaline solution was then precipitated with dilute hydro-

¹⁴ Staudinger and Breusch, *Ber.*, 62, 450 (1929).

chloric acid and the precipitate dissolved in alcohol. The solution deposited a considerable amount of colorless prisms melting at 225°. Since most of this product failed to crystallize, it was dissolved in excess of ammonium hydroxide, the solution diluted several times and then concentrated to its original volume on the hot-plate, when part of the material separated as an oil. The fraction which remained in solution was precipitated with dilute hydrochloric acid and the precipitate dissolved in ethyl alcohol, from which colorless needles were obtained which melted at 245° after recrystallization. The fraction which was precipitated was also dissolved in alcohol and gave very fine colorless needles which after recrystallization melted at 285°. The portion which did not crystallize was then dissolved in ether and extracted with 0.25 *N* ammonium hydroxide solution. The extracted material was precipitated from the ammoniacal solution by dilute hydrochloric acid and dissolved in alcohol from which a considerable quantity of colorless rhombohedral prisms melting at 190° was deposited. From the ether solution, more of the 285° compound was obtained.

The compounds melting at 95 and 295°, respectively, were not obtained in sufficient quantities for macro analysis. The analyses of the other compounds and the solubility in hot 5% sodium hydroxide solution and hot 5% ammonium hydroxide solution are given in Table I. It will be seen that in general the oxidation products which were isolated have a complex structure. Only traces of benzoic acid and benzophenone were obtained. The compound melting at 146° was identified as *o*-dibenzoylbenzene, and gave no depression in melting point when mixed with a sample of this compound prepared by the oxidation of *o*-dibenzylbenzene. The other compounds have not as yet been identified.

TABLE I

ANALYSES AND SOLUBILITY DATA OF THE OXIDATION PRODUCTS OF 1,1,3-TRIPHENYL-3-METHYLHYDRINDENE

M. p. of compound, °C. (uncorr.)	Soly. in hot 5% NaOH soln.	Soly. in hot 5% NH ₄ OH soln.	Formula	Calculated		Found	
				C, %	H, %	C, %	H, %
120	Insol.	Insol.	C ₁₆ H ₁₂ O ₂	81.32	5.12	81.16	5.06
146	Insol.	Insol.	C ₂₀ H ₁₄ O ₂	83.88	4.93	83.73	4.96
190	Sol. ^a	Sol.	C ₂₃ H ₂₀ O ₂	84.10	6.14	83.99	6.19
225	Slightly ^b	Insol.	C ₂₁ H ₁₄ O ₃	80.23	4.49	79.98	4.49
245°	Sol.	Sol.	C ₂₄ H ₂₂ O ₄	76.97	5.93	76.92	5.89
279	Insol.	Insol.	C ₂₂ H ₁₆ O ₃	80.45	4.92	80.47	4.89
285 ^d	Sol.	Insol.	C ₁₆ H ₁₂ O ₂	81.32	5.12	81.14	5.09

^a The sodium salt is insoluble in concentrated NaOH solution. ^b Dissolves slowly in hot concentrated NaOH solution. ^c This compound may be α -methyl- α,γ,γ -triphenylglutaric acid. ^d The properties of this compound agree with those described for an anhydro derivative of β -benzoyl- α -phenylpropionic acid. Anschütz and Montfort, *Ann.*, 284, 5 (1895); Hann and Lapworth, *J. Chem. Soc.*, 85, 1362 (1904).

Polymerization of Asymmetrical Diphenylethylene.—Ten grams of the ethylene was dissolved in 75 cc. of benzene and treated with 4 g. of anhydrous stannic chloride at room temperature. The solution developed a light green color which faded to a light brown during the course of a day or two. After seven days at room temperature the solution was washed thoroughly with water, dried and concentrated. The product was dissolved in alcohol, from which the unsaturated dimer, 1,1,3,3-tetraphenyl-1-butene was obtained in 77% yield, the residue being unchanged ethylene. Heating the reaction mixture on the steam-bath decreased the yield.

A similar reaction was carried out at room temperature using benzene which had been partially saturated with dry hydrochloric acid. The same light green color ap-

peared initially, but after two hours the solution had become dark red, which color persisted for about a day and then faded to a light brown. Crystallization of the product from absolute alcohol gave a 90% yield of the saturated dimer, 1,1,3-triphenyl-3-methylhydrindene.

Rearrangement and Depolymerization of 1,1,3,3-Tetraphenyl-1-butene.—This compound in benzene solution is not rearranged under the influence of stannic chloride but is partially depolymerized. Five grams of the butene in 40 cc. of benzene was treated with 2 g. of stannic chloride, whereupon the solution acquired a light green color which persisted for about a day. After seven days at room temperature the solution was washed with water, dried and concentrated, and the product dissolved in alcohol, from which 80% of the butene was recovered. The residue was distilled in vacuum and gave 0.7 g. of asymmetrical diphenylethylene. No appreciable rearrangement was observed with stannic chloride in boiling benzene, toluene or xylene, but when 5 g. of the butene was added to 50 cc. of stannic chloride and the solution refluxed for one week, a 90% yield of the saturated isomer was obtained.

The rearrangement is effected readily at room temperature provided hydrochloric acid is present. Five grams of the butene was dissolved in 40 cc. of benzene which was partially saturated with dry hydrochloric acid gas and 2 g. of stannic chloride was added. The solution first became light green and then dark red, the latter color fading after a day to a light brown. The solution was allowed to stand for a week at room temperature and was then washed with water, dried and concentrated. The residue was crystallized from absolute alcohol and gave a 90% yield of the saturated isomer, triphenylmethylhydrindene.

Summary

The saturated dimer of asymmetrical diphenylethylene has been identified as 1,1,3-triphenyl-3-methylhydrindene by means of its oxidation products.

The preparation of triphenylmethylhydrindene from methyldiphenylchloromethane has been described, and the method shown to be of general application.

The influence of stannic chloride on the polymerization of diphenylethylene and on the rearrangement and depolymerization of 1,1,3,3-tetraphenyl-1-butene has been described.

A reaction mechanism has been postulated for the formation of fluorene derivatives from triarylmethyl halides and for the formation of hydrindene derivatives from alkylarylmethyl halides.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

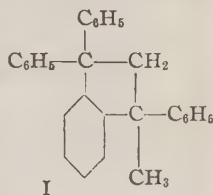
THE ABSORPTION SPECTRUM OF METHYLDIPHENYL- CHLOROMETHANE PLUS STANNIC CHLORIDE. THE PREPARATION OF 9,10-DIPHENYLPHENANTHRENE FROM TETRAPHENYLETHYLENE DICHLORIDE¹

By C. S. SCHOEPFLE AND J. D. RYAN

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In an earlier communication² it was shown that 1,1,3-triphenyl-3-methylhydrindene (I) is obtained in practically quantitative yield by adding anhydrous stannic chloride to a benzene solution of methyldiphenylchloromethane at room temperature. It was also shown that the reaction is a general one and can be used with other alkylarylmethyl halides and that other reagents such as antimony pentachloride, aluminum chloride, etc., can replace the stannic chloride. The reaction mechanism which was suggested postulated the formation of a quinonoid salt as an intermediate step, and in support of this assumption it was noted that the reaction is always accompanied by a transitory color and that the reagents used are those which are known to produce quinoidation of the triarylmethyl halides.



Preliminary absorption spectra measurements in the visible region failed to establish the identity of the intermediate colored compound or compounds since the point of maximum absorption was found to lie beyond the range of the visual apparatus. Spectrographic measurements of the absorption in the ultraviolet region have now been made which confirm the existence of a quinonoid modification of methyldiphenylchloromethane in the reaction mixture.

The quantitative absorption curves for methyldiphenylcarbinol, methyldiphenylchloromethane and asymmetrical diphenylethylene are shown in Fig. 1. (The curve for diphenylethylene was determined inasmuch as this compound is readily formed by loss of hydrogen chloride from methyldiphenylchloromethane.) The curves for the carbinol and the chloride

¹ This paper represents the second part of a dissertation submitted to the Graduate School by Mr. Ryan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

² Schoepfle and Ryan, *THIS JOURNAL*, 52, 4021 (1930).

show a marked similarity to those of triphenylcarbinol and triphenylchloromethane.³

An absolute quantitative curve could not be obtained in the case of the methyldiphenylchloromethane-stannic chloride mixture, due to the fact

that the concentration of the chloride drops and other compounds are formed as the reaction proceeds. However, the absorption of the solution in ethylene chloride was measured directly after adding the stannic chloride and the resulting curve is shown in Fig. 2 (Curve 1). This curve is entirely different from that of the chloride in the absence of stannic chloride, but is very similar in some respects to the quantitative absorption curves for the triphenylchloromethane-stannic chloride addition compound (Curve 2) and for triphenylmethyl acid sulfate (Curve 3). (The absorption curve of the latter compound has been determined by Anderson⁴ and is inserted here to facilitate comparison.) Since the quinonoid character of triphenylmethyl acid sulfate has been established,^{4,5} it follows from a comparison of the three curves that the band in Curve 1 with maximum frequency 2300 mm.⁻¹ is due to a quinonoid addition compound of methyldiphenylchloromethane.

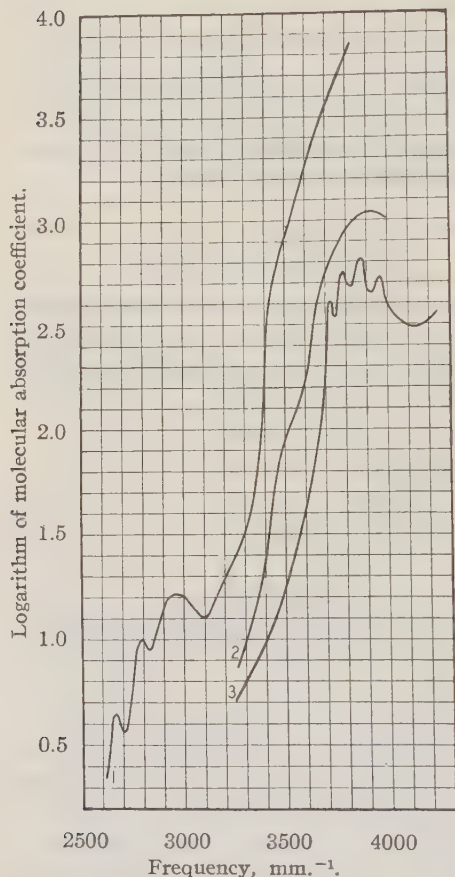


Fig. 1.—Curve 1, asymmetrical diphenylethylene in ether; Curve 2, methyldiphenylchloromethane in petroleum ether; Curve 3, methyl-diphenylcarbinol in ether.

The solution of methyldiphenylchloromethane and stannic chloride is at first red in color but after standing a short time the color changes to a greenish-red due to an increase

³ Anderson, *THIS JOURNAL*, **50**, 208 (1928).

⁴ Anderson, *ibid.*, **52**, 4567 (1930).

⁵ (a) Gomberg, *Ber.*, **40**, 1853 (1907); (b) Gomberg and Blicke, *THIS JOURNAL*, **45**, 1770 (1923).

in intensity of the absorption band with maximum frequency 1660 mm.^{-1} . A benzene solution of asymmetrical diphenylethylene and stannic chloride develops a pure green color and shows an absorption band at approximately this same frequency. It is possible that this band is due to the presence of a quinonoid form of 1,1,3,3-tetraphenyl-1-chlorobutane which may result from the addition of hydrogen chloride to 1,1,3,3-tetraphenyl-1-butene, inasmuch as diphenylethylene is known to polymerize in the presence of stannic chloride to give the latter compound. Attempts to prepare 1,1,3,3-tetraphenyl-1-chlorobutane from the corresponding butanol were unsuccessful, the butene being obtained instead.

Bergmann and co-workers⁶ have shown that compounds similar to 1,1,3,3-tetraphenyl-1-chlorobutane in the presence of stannic chloride split off a molecule of acid with ring closure to give hydrindene derivatives. Since the absorption measurements of the methyldiphenylchloromethane-stannic chloride mixture indicate the possibility that a quinonoid form of 1,1,3,3-tetraphenyl-1-chlorobutane may be present in addition to the quinonoid form of methyldiphenylchloromethane, no definite conclusion can be drawn from these measurements as to which of the two chlorides is the intermediate product in the formation of triphenylmethylhydrindene.

Attention was called in the previous paper² to the striking resemblances to be found in comparing the preparation of hydrindene derivatives from alkylarylchloromethanes and the preparation of fluorene derivatives from triarylchloromethanes. Another reaction analogous to these is the prepa-

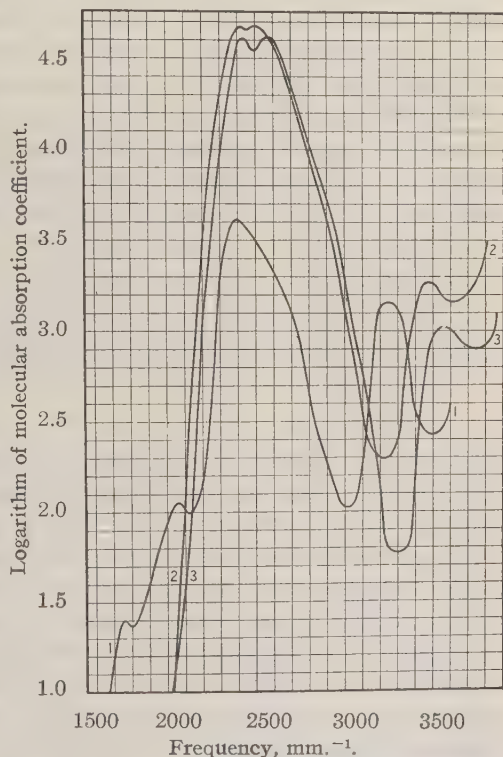
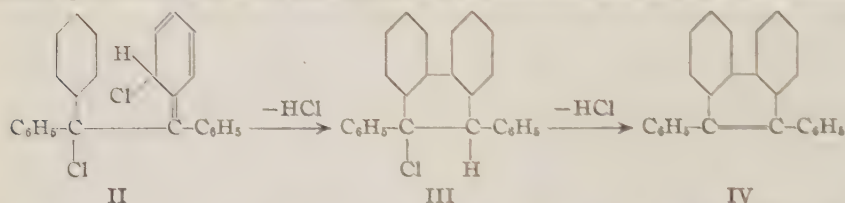


Fig. 2.—Curve 1, methyldiphenylchloromethane plus stannic chloride in ethylene chloride; Curve 2, triphenylchloromethane plus stannic chloride in ethylene chloride; Curve 3, triphenylmethyl acid sulfate in sulfuric acid (95%).

⁶ Bergmann, Taubadel and Weiss, *Ber.*, **64**, 1493 (1931).

ration of 9,10-diphenylphenanthrene (IV) from tetraphenylethylene dichloride. This reaction as carried out by Schmidlin and Von Escher⁷ consists in treating tetraphenylethylene dichloride with aluminum chloride in benzene or carbon disulfide solution, and according to Prins⁸ is an example of an intramolecular Friedel Crafts reaction. It has now been found that in solvents favoring quinoidation the aluminum chloride may be replaced with advantage by stannic chloride, so that in this respect the reaction differs from the usual Friedel Crafts reaction. A possible explanation of the reaction mechanism is that the ortho quinonoid modification of tetraphenylethylene dichloride (II) loses a molecule of hydrochloric acid to give a radical which rearranges to 9,10-diphenyl-9-chloro-(9,10-dihydrophenanthrene) (III), which compound then loses another molecule of hydrochloric acid to give 9,10-diphenylphenanthrene (IV). Or perhaps two rings become quinonoid and both molecules of hydrochloric acid are split off simul-



taneously. In general, a para quinonoid form reacts in preference to the corresponding ortho form but this need not hold for reactions in which a stable product can result from the ortho but not from the para modification.

Tetraphenylethylene dichloride dissolved in chloroform and treated with stannic chloride was found to give an intensely colored purple solution which gradually becomes colorless after a few hours, a 95% yield of 9,10-diphenylphenanthrene being obtained. The purple color is undoubtedly due to the formation of the quinonoid modification of tetraphenylethylene dichloride. This conclusion is supported by the fact that tetrakis-(dimethylaminophenyl)-ethylene adds chlorine directly to give a violet colored chloride⁹ to which Kehrmann¹⁰ and Recsei¹¹ assign a quinonoid configuration.

A study of the reaction of tetraphenylethylene dichloride and stannic chloride in various solvents showed that the character of the solvent has a marked effect on the formation of diphenylphenanthrene. In ethylene chloride, chloroform, nitrobenzene and benzonitrile, a quinonoid salt is produced, as manifested by the development of an intense purple color, and excellent yields of diphenylphenanthrene are obtained. On the other

⁷ Schmidlin and von Escher, *Ber.*, **43**, 1153 (1910).

⁸ Prins, *J. prakt. Chem.*, [2] **89**, 438 (1914).

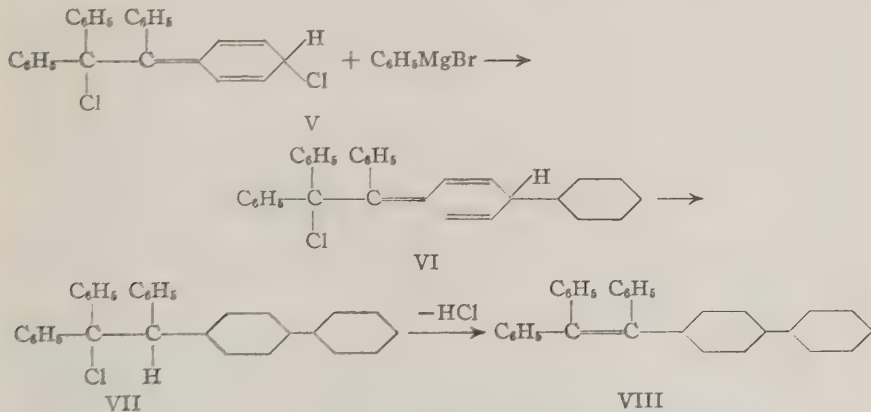
⁹ Wizinger, *Ber.*, **60**, 1383 (1927).

¹⁰ Kehrmann, *ibid.*, **60**, 1913 (1927).

¹¹ Recsei, *ibid.*, **60**, 2383 (1927); see also Madelung and Oberwegner, *ibid.*, **60**, 2469 (1927).

hand, under the same conditions no color is developed in benzene, carbon tetrachloride or carbon disulfide and little or no diphenylphenanthrene is obtained, most of the tetraphenylethylene dichloride being recovered unchanged. Since color develops in polar solvents and not in non-polar solvents, it is evident that the former favor quinoidation.¹² And while the fact that the reaction proceeds only in solvents which favor quinoidation does not necessarily indicate that a quinonoid salt must be an intermediate step in the preparation of diphenylphenanthrene, it does nevertheless lend plausibility to such an hypothesis.

Further support for the suggested mechanism is found in the reaction of tetraphenylethylene dichloride and phenylmagnesium bromide. Norris¹³ carried out this reaction in the hope of preparing hexaphenylethane, but instead obtained tetraphenylethylene and 4-phenyltetraphenylethylene. No attempt was made to interpret the mechanism of formation of the latter compound, and yet it can be logically explained by the assumption that the para quinonoid modification of tetraphenylethylene dichloride (V) reacts with phenylmagnesium bromide. The resulting product (VI) rearranges to 1,1,2-triphenyl-2-biphenyl-1-chloroethane (VII), which then yields 4-phenyltetraphenylethylene (VIII) by loss of a molecule of hydrochloric acid.



Other Grignard reactions which substantiate this hypothesis will be discussed in a separate communication.

9,10-Diphenylphenanthrene may also be prepared in 25% yield by treating tetraphenylethylene in chloroform solution with bromine at -40° in the presence of stannic chloride. The reaction is of interest since the addition of bromine to the double bond must be postulated as an intermediate step, and tetraphenylethylene has repeatedly been cited as a classi-

¹² See also Diltney, *J. prakt. Chem.*, [2] 109, 273 (1925).

¹³ Norris, Thomas and Brown, *Ber.*, 43, 2955 (1910).

cal example of a compound which would not add bromine although it does add chlorine, and also sodium.

The measurements of the absorption spectra were made with the assistance of Dr. L. C. Anderson of this Laboratory to whom we wish to express our appreciation.

Experimental

Absorption Spectra Data.—For the measurement of quantitative absorption spectra in the ultraviolet region, a Judd-Lewis sectorphotometer and a Hilger quartz spectrograph, size C, were employed. Absorption spectra in the visible region were determined by the use of a Nutting photometer and a Hilger constant wave length spectrometer. The procedure was that described by Anderson and Gomberg.¹⁴

Asymmetrical diphenylethylene was prepared by the action of 30% sulfuric acid on methyldiphenylcarbinol¹⁵ and was fractionated several times under reduced pressure; b. p. 148° at 17 mm.; f. p. 8°.

Methyldiphenylcarbinol was prepared by the action of phenylmagnesium bromide upon ethyl acetate and was purified by recrystallization from ether plus petroleum ether, m. p. 81°.

Methyldiphenylchloromethane could not be isolated in crystalline form. It was prepared by saturating a petroleum ether solution of the corresponding carbinol with dry hydrogen chloride at 0° in the presence of anhydrous calcium chloride. The calcium chloride was filtered off and a stream of dry air passed through the solution under reduced pressure at 0° to remove the solvent and excess hydrogen chloride. An analysis of the residual oil gave 98% of the theoretical amount of chlorine, indicating that no appreciable decomposition had taken place. Preliminary measurements showed that hydrogen chloride had no effect on the absorption of methyldiphenylchloromethane when dissolved in petroleum ether; therefore the solutions used for obtaining the absorption (Fig. 1, Curve 2) were made in the following manner. A weighed amount of the carbinol was dissolved in about 5 cc. of pure petroleum ether and the solution cooled and diluted to 25 cc. with cold petroleum ether saturated with hydrogen chloride, after which anhydrous calcium chloride was added and the mixture allowed to stand overnight at 0°. Five cc. of the solution was then pipetted off, diluted with petroleum ether to the proper concentration and the absorption measured. A sample which had been kept for three days at 0° gave results identical with those obtained with a sample which had been allowed to stand for eighteen hours.

The solution used for obtaining the absorption of methyldiphenylchloromethane plus stannic chloride (Fig. 2, Curve 1) was prepared in a similar manner using ethylene chloride as the solvent, except that the final dilution was made with ethylene chloride which was saturated with hydrogen chloride and contained 1% by volume of anhydrous stannic chloride. The entire curve was obtained with a 0.0025 molar solution since the absorption differs somewhat with different concentrations.

9,10-Diphenylphenanthrene.—Tetraphenylethylene dichloride was prepared by passing dry chlorine through a carbon tetrachloride solution of tetraphenylethylene at 0°¹⁶ and recrystallizing the product thus obtained from a mixture of carbon disulfide and ethyl acetate.¹⁷ One gram of the dichloride was dissolved in 40 cc. of pure chloroform and cooled in a freezing mixture to a temperature of -5 to -10°. Two cc. of

¹⁴ Anderson and Gomberg, *THIS JOURNAL*, **50**, 203 (1928).

¹⁵ Lebedev, Andreevskii and Matiushkina, *Ber.*, **56**, 2349 (1923).

¹⁶ Finkelstein, *Ber.*, **43**, 1534 (1910).

¹⁷ Norris, *THIS JOURNAL*, **38**, 707 (1916).

anhydrous stannic chloride was added, whereupon the solution assumed a deep purple color which gradually faded. After a few hours, the solution became colorless and was then washed thoroughly with water, dried and concentrated. Crystallization of the solid residue from absolute alcohol gave 9,10-diphenylphenanthrene in 90–95% yield, m. p. 235°. When mixed with an authentic specimen, no lowering in melting point was observed. Schmidlin and von Escher,⁷ who carried out this reaction using aluminum chloride, obtained a 60% yield. At higher temperatures the reaction proceeds more rapidly but chlorinated products are formed which decrease the yield of diphenylphenanthrene.

Repetition of the experiment described above using ethylene chloride, nitrobenzene or benzonitrile as the solvent instead of chloroform gave a similar result. When benzene, carbon disulfide or carbon tetrachloride was used, however, no color was observed and only a trace of diphenylphenanthrene was obtained. About 60–70% of the tetraphenylethylene dichloride was recovered unchanged, along with an appreciable amount of chlorinated products.

Diphenylphenanthrene was also prepared from tetraphenylethylene and bromine. Five grams of tetraphenylethylene was dissolved in 100 cc. of chloroform and treated with 7 cc. of anhydrous stannic chloride. The green solution thus obtained was cooled to –40° and 2.4 g. (1 mole) of bromine was added. A deep purple color developed which had not disappeared after two hours, whereupon the solution was treated with a calcium chloride freezing mixture. Addition of the aqueous solution resulted in the disappearance of the purple color but considerable bromine was still present which was removed by washing with bisulfite solution. When the chloroform layer was dried and concentrated, a crystalline product was obtained which after repeated crystallization gave a 25% yield of pure 9,10-diphenylphenanthrene melting at 235°. The remainder of the material consisted of unchanged tetraphenylethylene and a small amount of brominated products. At room temperature a mixture of tetraphenylethylene and various bromination products of tetraphenylethylene and diphenylphenanthrene was obtained.

When the reaction was carried out in ethylene dichloride, the results were similar to those obtained in chloroform, but in carbon disulfide or carbon tetrachloride the purple color was not developed and little or no diphenylphenanthrene was obtained.

1,1,3,3-Tetraphenyl-1-butanol.—Five grams of finely ground β,β -diphenylbutyrophenone prepared by the method of Kohler¹⁸ was added to an ether solution of phenylmagnesium bromide made from 3 g. of magnesium. The mixture was refluxed for one hour, then decomposed with ice and acid, and the ethereal layer washed, dried and concentrated. The solid residue crystallized from alcohol in plate-like prisms melting at 124–125°; yield, 75%. The carbinol is readily soluble in the common organic solvents except petroleum ether.

Attempts to prepare the corresponding chloride, 1,1,3,3-tetraphenyl-1-chlorobutane, by saturating a benzene solution of the carbinol with dry hydrogen chloride at –5° in the presence of anhydrous calcium chloride gave instead a quantitative yield of 1,1,3,3-tetraphenyl-1-butene.

The butene is also obtained if the butanol is dissolved in glacial acetic acid at room temperature and a few drops of concentrated sulfuric acid added. However, if 1 g. of the powdered butanol is treated with 25 cc. of concentrated sulfuric acid, 1,1,3-triphenyl-3-methylhydrindene is formed in approximately 25% yield, the remaining product consisting principally of asymmetrical diphenylethylene with a small amount of tetraphenylbutene. The triphenylmethylhydrindene appears to be formed from the carbinol and not by rearrangement of the butene, for when 3 g. of the butene was treated

¹⁸ Kohler, *Am. Chem. J.*, **31**, 657 (1904); *ibid.*, **38**, 558 (1907).

with 15 cc. of concentrated sulfuric acid and the mixture allowed to stand for forty-eight hours at room temperature, the product obtained proved to be unchanged butene, a small amount of diphenylethylene, and water-soluble sulfonated products. No triphenylmethylhydrindene could be isolated. When a similar mixture was allowed to stand for six weeks, only about 0.1 g. of the hydrindene was obtained, although Bergmann and Weiss¹⁹ state that the hydrindene can be readily prepared from the butene by means of sulfuric acid.

Summary

1. The quantitative absorption spectra of the following compounds have been obtained: asymmetrical diphenylethylene, methyldiphenylcarbinol, methyldiphenylchloromethane, methyldiphenylchloromethane plus stannic chloride, and triphenylchloromethane plus stannic chloride.

2. The preparation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and stannic chloride has been investigated and the effect of polar and non-polar solvents noted.

3. A reaction mechanism involving quinoidation has been postulated to explain the formation of 9,10-diphenylphenanthrene from tetraphenylethylene dichloride and also the formation of 4-phenyltetraphenylethylene from tetraphenylethylene dichloride and phenylmagnesium bromide.

¹⁹ Bergmann and Weiss, *Ann.*, **480**, 49 (1930).

